# Intermediate valence behavior in $CeCo_9Si_4$

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**Abstract**

The novel ternary compound $CeCo_9Si_4$ has been studied by means of specific heat, magnetisation, and transport measurements. Single crystal X-ray Rietveld refinements reveal a fully ordered distribution of Ce, Co and Si atoms with the tetragonal space group *I4/mcm* isostructural with other $RCo_9Si_4$. The smaller lattice constants of $CeCo_9Si_4$ in comparison with the trend established by other $RCo_9Si_4$ is indicative for intermediate valence of cerium. While $RCo_9Si_4$ with $R$ = Pr, ... Tb, and Y show ferromagnetism and $LaCo_9Si_4$ is nearly ferromagnetic, $CeCo_9Si_4$ remains paramagnetic even in external fields as large as 40 T, though its electronic specific heat coefficient ($\gamma \simeq 190\,\mathrm{mJ/mol\,K^2}$) is of similar magnitude as that of metamagnetic $LaCo_9Si_4$ and weakly ferromagnetic $YCo_9Si_4$.

*Key words:*
$CeCo_9Si_4$, Intermediate Valence, High Field Measurement

The ordered ternary rare-earth cobalt silicon phase with composition 1:9:4 attracted our attention mainly because of the extraordinary magnetic properties of $LaCo_9Si_4$ which is a strongly exchange enhanced Pauli paramagnet and exhibits an itinerant metamagnetic phase transition at about 3.5 T for $H||c$ and 6 T for $H\perp c$, which is the lowest value ever found for rare earth intermetallic compounds [1]. Related isostructural $RCo_9Si_4$ with $R$ = Pr, Nd, Gd, Dy and also Y are ferromagnetic (see Refs. [2,3]) with relatively low $T_C \sim 20 - 50$ K. This report is on the exceptional behavior of $CeCo_9Si_4$ among the ferromagnetic (FM) or almost FM $RCo_9Si_4$ compounds.

Polycrystalline samples of $CeCo_9Si_4$ and related $RCo_9Si_4$ were synthesized by induction melting of pure elements ($R$ 3N, Co 4.5N, Si 6N) under protective argon atmosphere and subsequent annealing at

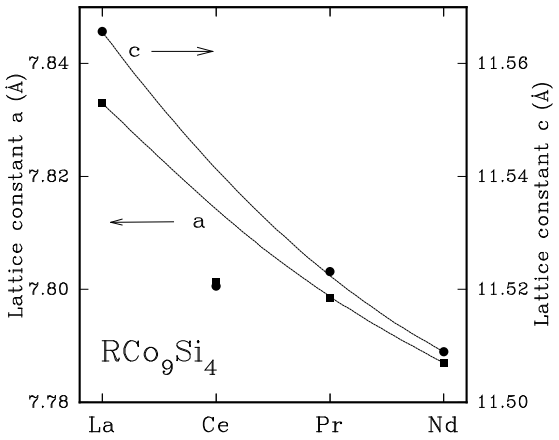


Fig. 1. Comparison of lattice parameters $a$ (squares) and $c$ (circles) of some $RCo_9Si_4$ compounds; dashed lines guides to the eye.

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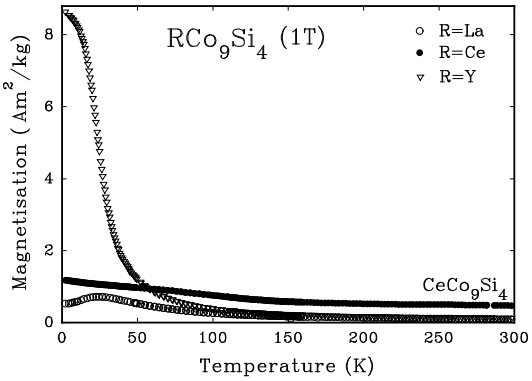


Fig. 2. Temperature dependent magnetisation $M(T)$ measured at 1T of $CeCo_9Si_4$ and for comparison $LaCo_9Si_4$ and $YCo_9Si_4$.

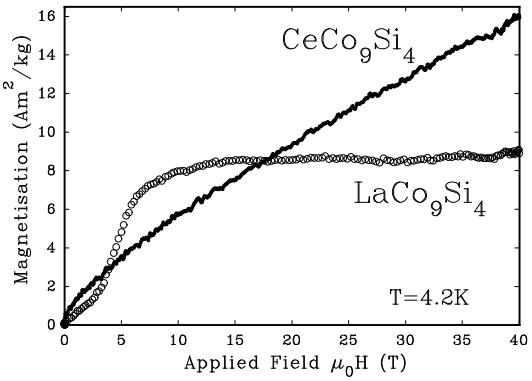


Fig. 3. High-field magnetisation measurements $M(H)$ on $CeCo_9Si_4$ and $LaCo_9Si_4$ performed at 4.2 K.

1050°C for one week. The crystal structure was determined by means of single crystal X-ray diffraction ($R_{F^2}$ = 2.3%) revealing, analogous to $CeNi_9Si_4$ [4], a fully ordered distribution of Ce, Co and Si atoms with the $LaFe_9Si_4$-type [5] (space group $I4/mcm$). The lattice parameters are $a = 7.801(1)$ Å and $c = 11.521(2)$ Å at room temperature.

The comparison of the lattice parameters of $RCo_9Si_4$ with R = La, Ce, Pr, Nd shown in Fig. 1 reveals a significant negative deviation of the $CeCo_9Si_4$ data from the common trend. The smaller lattice constants of $CeCo_9Si_4$ indicates an intermediate valence state inbetween the magnetic trivalent $4f^1$ and the non-magnetic tetravalent $4f^0$ state due to hybridization of $4f$ and conduction band states. Intermediate valence close to tetravalence is corroborated by the magnetisation data shown in Fig. 2 where the Curie-Weiss component expected for $Ce^{3+}$ ions is not observed. The dc susceptibility measurement in fact reveals an almost temperature independent paramagnetic susceptibility for $CeCo_9Si_4$, while $LaCo_9Si_4$ exhibits a more pronounced temperature dependence, typical for a spin fluctuation system, and all other $RCo_9Si_4$ are ferromagnetic below 20–50 K (see the $YCo_9Si_4$ data shown in Fig. 2 as one example). The small off-set of the room temperature magnetic moment of $CeCo_9Si_4$ as compared with $LaCo_9Si_4$ and $YCo_9Si_4$ in Fig. 2 is due to a contribution from traces of unreacted free Co which is also visible in the M(H) data (see Fig. 3). The Pauli-susceptibility $\chi_0$ estimated from $M/H$ at 40 T is about $5 \times 10^{-7}$ m$^3$/kg, slightly smaller than $8.2 \times 10^{-7}$ m$^3$/kg given in Ref. [1] for $LaCo_9Si_4$.

Motivated by the metamagnetism observed for $LaCo_9Si_4$ high-field magnetisation $M(H)$ measurements have been carried out up to 40 T in pulsed fields (see Ref.[6] for details of the setup) on $CeCo_9Si_4$ and $LaCo_9Si_4$ for comparison. Apart from a small hysteresis at low fields due to the above mentioned Co impurities, $CeCo_9Si_4$ shows a rather perfectly linear paramagnetic field dependence reaching $2\,\mu_B$/f.u. at $B_{max} = 40$ T, whereas the magnetic moment of the field induced FM state of $LaCo_9Si_4$ saturates already above about 8 T at approximately $1.1\,\mu_B$/f.u.

The obviously more stable paramagnetic state of $CeCo_9Si_4$ with respect to the appearance of metamagnetism is most likely due to $d$-band filling caused by hybridized $4f$ states of cerium being close to tetravalence. Thus, one expects a reduction of spin-fluctuation mass enhancement which however may be partly compensated by contributions due to Ce valence fluctuations. The latter is supported by the specific heat data (not shown) where the linear electronic specific heat coefficient of $CeCo_9Si_4$, the Sommerfeld value $\gamma \simeq 190$ mJ/molK$^2$, is slightly lower than that of nearly magnetic $LaCo_9Si_4$, where $\gamma \simeq 200$ mJ/molK$^2$. The comparison of the temperature dependent resistivities $\rho(T)$, on the other hand (not shown), indicates for both a Fermi liquid behavior with $\rho(T) = \rho_0 + AT^2$, however, with a significantly lower $A$-coefficient for $CeCo_9Si_4$ as compared to $LaCo_9Si_4$ [7].

We conclude that $CeCo_9Si_4$ exhibits intermediate valence with Ce being close to a non-magnetic tetravalent state where $4f$ states hybridize with the conduction bands and thereby weaken the magnetic correlations among $d$-electrons as compared to other $RCo_9Si_4$.

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